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ABSTRACT

The loss of sheet strength associated with the use of recycled fibers limits their utility as a general fiber source. Carboxymethyl substitution is well known to strengthen sheets made from both cotton and wood pulps. We have investigated the mechanism utilizing the network theory of paper using equations proposed by D. Page et al. and data previously reported in the literature. We have determined that carboxymethylation affected the ability of the fibers to conform to each other thereby increasing the relative bonded area of the fibers in the paper sheet. Carboxymethylated fibers were also less likely to be reduced in length during refining. These two effects together accounted for the increase in sheet strength with carboxymethylation. The increase in relative bonded area alone accounted for 70% of the improvement in strength. Based on this analysis we hypothesize that selective placement of acid groups near the surface of pulp fibers will significantly improve the strength of recycled fibers. A novel chemical approach to upgrade the strength of recycled pulps is proposed.

INTRODUCTION

The use of recycled fibers is an ever-expanding concern of today's papermaker. The American Forest & Paper Association has identified recycling as a research priority for the industry, citing fiber bonding as a specific area requiring research [1]. The Page Equation [2] can be used to separate fiber bonding into its components of specific bond strength and relative bonded area (RBA). Ellis and Sedlachek [3] used the Page Equation and reported that the loss of strength with recycling is due to a loss of bonded area. Myers [4] has demonstrated that recycled fibers cannot regain their full papermaking potential through refining alone and that a more aggressive approach is required. These results, when coupled with a reevaluation of historic data presented here, suggest a novel method of upgrading the strength of recycled papers.

It has been established that carboxymethyl substitution enhances the strength of both cotton and wood pulps [5-8]. The improved strength was attributed to increased plasticity of the fibers, increased bonding, increased bonded area, or increased aggregate bond strength [5,6]. The analysis presented here indicates that the increase in strength was due to an increase in RBA. The result is expected from Scallan's explanation of the role of acidic groups in fiber swelling [9]. Counter ions to acidic groups in fibers induce an osmotic pressure and cause the fibers to swell. Swollen fibers are more conformable and bonded area is increased. Scallan's explanation is confirmed by Talwar [6] who found that the strength increase with carboxymethylation was realized only when the acidic groups were deprotonated. Increased acidic group content can increase RBA. The controlled introduction of acidic groups into recycled fibers can therefore represent a method to upgrade the strength of recycled papers.

Numerous methods exist to introduce acidic groups on cellulose. One pathway is through direct oxidation of cellulose with nitrogen dioxide, ozone, hydrogen peroxide, or oxygen [10]. Other pathways include addition of sulfonic acid groups to lignin [11], grafting of carboxylic acids to cellulose [5], and the formation of free radicals with devices such as electron beams [12].

DATA ANALYSIS

Ellis and Sedlachek [3] have used a form of the Page Equation to separate factors which contribute to the strength of papers made with recycled fiber. The Page Equation is given in Equation (1).

$$1/T = 9/8Z + (12gC/PLbRBA) \qquad (1)$$

RBA can be calculated from the scattering coefficients of the sheets using Equation (2).

$$RBA = (S_0 - S)/S_0 \qquad (2)$$

Substituting Equation (2) into Equation (1) and rearranging produces Equation (3), which relates the tensile properties of the sheet to scattering coefficients.

$$[1/T - 9/8Z]^{-1} = b/g - (b/gS_0)S \qquad (3)$$

Equation (3) shows that the scattering coefficient of an unbonded sheet (used to calculate RBA) and the specific bond strength can be determined from readily measured quantities.

ANALYSIS OF EXPERIMENTAL RESULTS

Walecka produced carboxymethyl cellulose by treating paper grade cotton fibers with chloroacetic acid. Walecka performed several beater curves on these pulps and recorded strength data [5,13]. The data collected by Walecka were reevaluated using Equation (3). Walecka's data were suitable for this analysis with the exception that TAPPI opacity was recorded, not scattering coefficient. However, Talwar [6] followed Walecka and used the same pulp and techniques. Talwar's unpublished data [14] showed that degree of carboxymethyl substitution did not alter the reflectivity of the sheets. It was judged acceptable to use Talwar's reflectivity to determine scattering coefficients from Walecka's TAPPI opacities using a suitable table [15].

Figure 1 shows the relationship between freeness and breaking length for pulps studied by Walecka. Not all data are shown. We tested the results by fitting the data to a model containing linear and quadratic terms in freeness and acid content. The statistics showed that the acid content was significant at the 95% confidence level. For each acid content the tensile strength versus freeness curve was interpolated to 500 freeness. The result is Figure 2, which clearly demonstrates the impact of acid content on strength. The tensile strength is improved by 44% over the range of acid contents studied. The maximum effect appears to be at an acid content of 200 meq/kg.

Since the purpose of this analysis is to understand how the acid content improves the tensile strength, in the context of Equation (1), we must explore the effect of acid content on each of the terms of the Page Equation. The effect of acid content on zero span tensile strength is shown in Figure 3. Although Walecka did not measure fiber lengths, the pulps were fractionated on a Bauer-McNett, and we were able to use these results to estimate fiber length [16]. The effect of acid content on fiber length is shown in Figure 4. Increases in acid content countered the impact of refining on fiber length reduction.

We plotted the reciprocal of L*[1/T-9/8Z] versus scattering coefficient and the result is shown in Figure 5. The L term was included in the Page Parameter because a reasonable estimate of fiber length was available. Equation (3) predicts that this plot will be a single straight line if the data can be represented by the same fiber-to-fiber specific bond strength and the same scattering coefficient for unbonded fibers. The fit in Figure 5 is a straight line with an R^2 of 0.77. We tested the data shown in Figure 5 for dependency on acid content and found that this factor was not significant at the 95% confidence level. We conclude that the Page analysis has accounted for the observed effect of acid content. Since the fiber-to-fiber specific bond strength is equivalent for all the levels of acid content, we conclude that the principle effect of acid content is to increase the relative bonded area at any level of refining.

Since zero span breaking length, fiber length, and RBA all change with acid content, it is instructive to calculate the relative contributions of these to the observed rise in breaking length. The maximum beneficial effects of acid groups appears to occur at a level of around 200 meq/kg. This acid content was then compared to the control pulp for calculation of relative contributions. The values for breaking length, zero span breaking length, fiber length, and RBA at 500 freeness were inserted into Equation (1) to establish a value for the unknown quantities. The known values were then inserted into Equation (1) and varied one at a time from low to high levels to determine the relative contribution of each quantity. The increase in breaking length from low to high acid content was +30%. The relative contribution of the increase in zero span breaking length to this change in tensile strength was calculated to be 9%, fiber length accounting for 20%, and the increase in RBA represented 71% of the increase in tensile strength.

DISCUSSION/CONCLUSIONS

This analysis of historical data demonstrates that introduction of carboxylate groups in fibers increases the relative bonded area. We believe the mechanism of this effect is an increased conformability of the fibers due to increased fiber swelling. Introduction of acidic groups into recycled fibers, from direct oxidation or grafting, appears to offer a path to upgrade the strength of recycled papers.

There are many chemical treatments which can introduce acid groups into wood pulp. From a practical point of view, ozone and hydrogen peroxide perhaps offer the best opportunity to introduce acid groups in fully bleached pulps. These chemicals are already being employed in the bleaching of recycled fibers. Therefore, experiments to establish the optimum conditions for direct oxidation of the fiber cellulose will be important to the design and operation of bleaching operations. Although ozone and peroxide will introduce acid groups into unbleached pulps, another method is possible. The introduction of sulfonic acid groups may eliminate the cellulose damage expected from other treatments.

NOTATION

T	tensile breaking length
Z	zero span breaking length
C	fiber coarseness
P	fiber perimeter
L	fiber length
b	fiber-to-fiber specific bond strength
RBA	relative bonded area
g	gravitational constant
S_0	scattering coefficient of unbonded sheet
S	scattering coefficient of paper sheet
g	12gC/PL
Page Parameter	$[1/T-9/8Z]^{-1}$

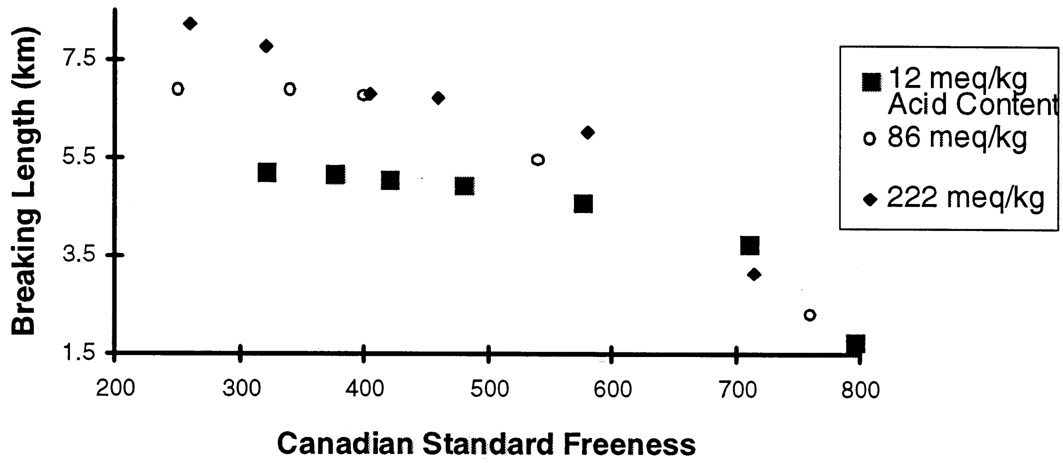

FIGURE 1. The effect of refining on tensile strength.

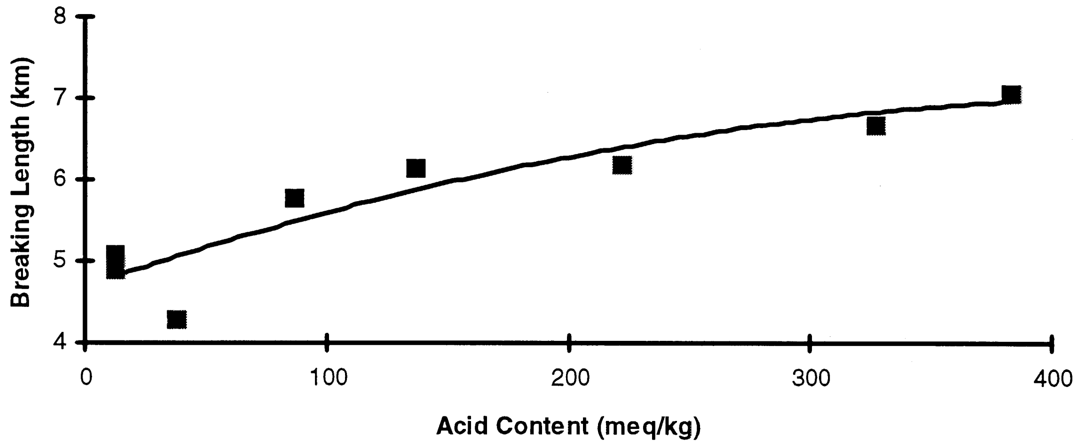

FIGURE 2. The effect of acid content on breaking length at 500 CSF.

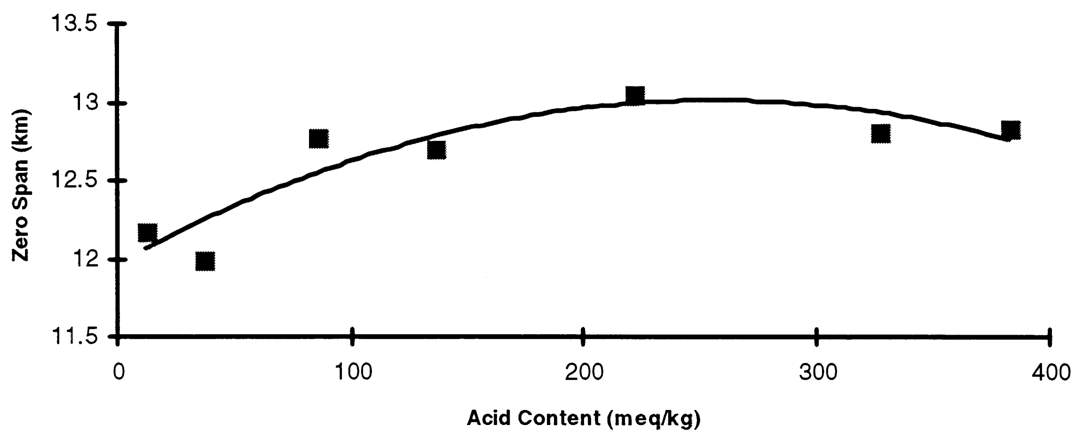

FIGURE 3. Zero span versus acid content at 500 CSF.

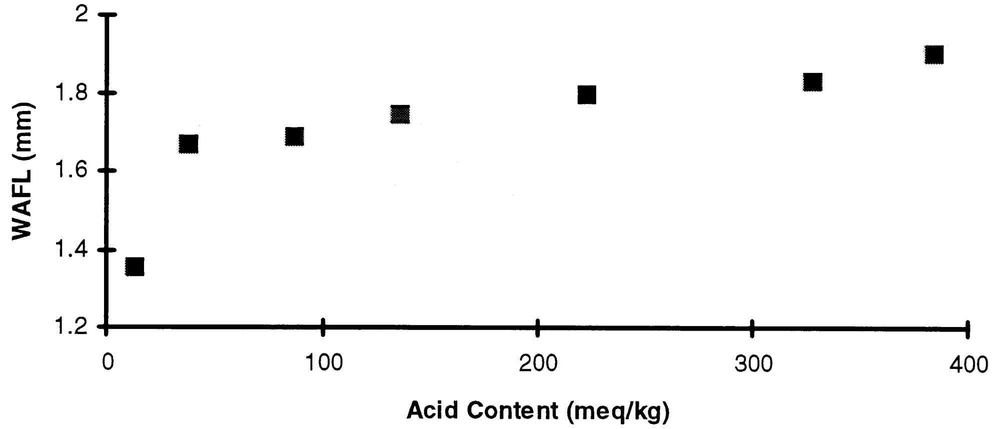

FIGURE 4. Weight average fiber length vs acid content at 500 CSF.

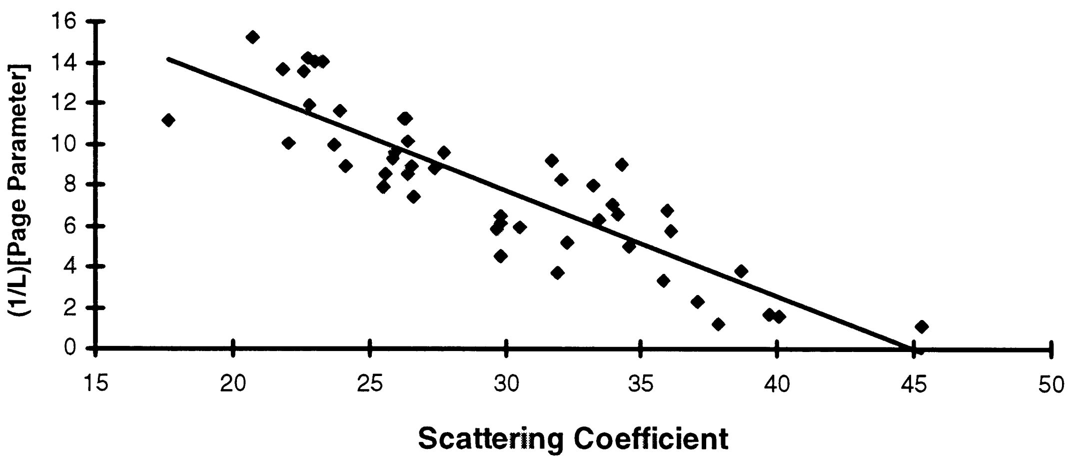

FIGURE 5. Page Plot for entire data set.

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